

WHAT IS CLAIMED IS:

- 5 1. A cement powder comprising reactive tricalcium phosphate nanoparticles and other ingredients required to form a cementous material. 112
2. The cement powder according to claim 1, wherein the cement powder comprises at least 50% by weight of the reactive tricalcium phosphate nanoparticles.
- 10 3. The cement powder according to claim 1, wherein the cement powder has a calcium:phosphate molar ratio of not over about 1.5:1.
4. The cement powder according to claim 1, wherein the reactive tricalcium phosphate nanoparticles have an average size of less than 1 micrometer.
- 15 5. The cement powder according to claim 4, wherein at least about 85% by weight of the reactive tricalcium phosphate nanoparticles have an average size of less than about 500 nanometers.
- 20 6. The cement powder according to claim 1, wherein the other ingredients required to form a cementous material comprise a carbonate salt having a counterion selected from the group consisting of ammonia, a member of group IA or group IIA, and mixtures thereof, and a phosphate salt having a counterion selected from the group consisting of ammonia, a member of group IA or group IIA, and mixtures thereof.
- 25 7. The cement powder according to claim 6, wherein the counterion is calcium and the phosphate salt is calcium bis(dihydrogenphosphate) monohydrate.
- 30 8. The cement powder according to claim 7, wherein the reactive tricalcium phosphate nanoparticles are present in an amount between about 50% and 90%, calcium carbonate is present in an amount between about 0% and 25%, and calcium bis(dihydrogenphosphate) monohydrate is present in an amount between about 0% and 25%, all in percent by weight of the cement powder.

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(b) $\frac{d}{dt} \left(\frac{\partial L}{\partial v^i} \right) = \frac{\partial L}{\partial x^i}$

18. The cement paste according to claim 17, wherein the lubricating liquid comprises a phosphate salt having a counterion selected from the group consisting of ammonia, a member of group IA or IIA, and mixtures thereof, and polyacrylic acid or a salt of polyacrylic acid having a counterion selected from the group consisting of ammonia, a member of group IA or IIA, and mixtures thereof.

19. The cement paste according to claim 18, wherein the polyacrylic acid or a salt of polyacrylic acid has a number average molecular weight of between about 1000 and 1,000,000.

20. The cement paste according to claim 19, wherein the polyacrylic acid or a salt of polyacrylic acid has a number average molecular weight of between about 30,000 and about 90,000.

21. The cement paste according to claim 18, wherein the polyacrylic acid or a salt of polyacrylic acid has a number average molecular weight of about 60,000.

22. The cement paste according to claim 18, wherein the phosphate salt comprises ammonium phosphate, or sodium phosphate tribasic, or a mixture thereof, and the polyacrylate salt comprises sodium polyacrylate.

23. The cement paste according to claim 19, wherein the lubricating liquid comprises ammonium phosphate in an amount of between about 0 and 2 molar, and sodium polyacrylate in an amount of between about 0% and 20% by weight of the liquid solution.

24. The cement paste according to claim 15, comprising lubricating liquid in an amount of from about 0.2 ml to about 0.23 ml per gram of the cement powder.

25. The cement paste according to claim 15, comprising a filler.

26. The cement paste according to claim 15, comprising a bioactive agent.

27. The cement paste according to claim 26, wherein the bioactive agent comprises a growth factor.

28. A biocompatible cured cement comprising the cured form of a cement paste comprising a lubricating liquid which is intermixed with a cement powder that includes reactive tricalcium phosphate nanoparticles and other ingredients required to form a cementous material.

29. The cured cement according to claim 28, wherein the cured cement is bioabsorbable.

30. The cured cement according to claim 28, having a structure having an X-ray diffraction pattern that is more similar to the X-ray diffraction pattern of α -TCP than to the X-ray diffraction pattern of hydroxyapatite.

31. The cured cement according to claim 28, having a calcium:phosphate molar ratio of not over about 1.5:1.

32. The cured cement according to claim 28, having compressive strength of at least about 40 MPa at a time of 10 minutes after start of cure.

33. The cured cement according to claim 28, having a compressive strength of at least about 80 Mpa at a time of 12 hours after start of cure.

34. A method of making a cement powder containing reactive tricalcium phosphate nanoparticles, the method comprising forming the reactive tricalcium phosphate nanoparticles by precipitation from solution; and intermixing the nanoparticles with other ingredients required to form a cementous material.

35. The method according to claim 34, wherein the step of forming the reactive tricalcium phosphate nanoparticles comprises:

forming one or more aqueous solutions from which tricalcium phosphate can be precipitated;

precipitating tricalcium phosphate from the aqueous solution or solutions;

separating the precipitated tricalcium phosphate from the liquid portion of the solution;

drying the precipitated tricalcium phosphate;

sintering the dried tricalcium phosphate;
rapidly cooling the sintered tricalcium phosphate; and
reducing the cooled, sintered tricalcium phosphate to
nanoparticles having an average size of less than 1 micrometer.

5 36. The method according to claim 35, wherein the step of
forming one or more aqueous solutions from which tricalcium
phosphate can be precipitated comprises forming one of the solutions
so that it contains sodium sulfate.

10 37. The method according to claim 36, wherein the sodium
sulfate is present in an amount sufficient to prevent at least some of the
tricalcium phosphate that is formed during the precipitation from
converting to hydroxyapatite.

15 38. The method according to claim 35, wherein the solutions
that are formed comprise calcium and phosphorous in a molar ratio of
not over about 1.5:1.

 39. The method according to claim 38, wherein the step of
forming the reactive tricalcium phosphate nanoparticles comprises:

20 forming one or more aqueous solutions from which tricalcium
phosphate can be precipitated by forming a 1.0 M solution of calcium
nitrate in water, and forming a 1.33 M solution of ammonium
orthophosphate monohydrate in water;

precipitating tricalcium phosphate from the aqueous solution by
intermixing the calcium nitrate solution and the ammonium
orthophosphate monohydrate solution, and then by adding
25 concentrated ammonium hydroxide solution while the mixture is stirred
and heated to about 106°C;

separating the precipitated tricalcium phosphate by filtering, and
then washing the precipitated tricalcium phosphate with a solution of
0.18 M sodium sulfate;

30 drying the precipitated tricalcium phosphate by placing the
precipitated tricalcium phosphate in a drying oven at about 650°C for a
time of from about 1 to 2 hours;

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sintering the dried tricalcium phosphate at a temperature of about 1425°C for a time of from about 1 to 2 hours;

rapidly cooling the sintered tricalcium phosphate at a cooling rate of at least about 1000°C per minute; and

5 reducing the cooled, sintered tricalcium phosphate to nanoparticles having an average size of less than 1 micrometer by crushing or grinding.

40. The method according to claim 36, wherein the step of
10 reducing the cooled, sintered tricalcium phosphate to nanoparticles having an average size of less than 1 micrometer by crushing or grinding comprises crushing or grinding in a ball mill, pebble mill, rod mill, tube mill, compartment mill, tumbling mill, stirred ball mill or vibrating mill.

41. The method according to claim 40, wherein the ball mill,
15 pebble mill, rod mill, tube mill, compartment mill, tumbling mill, stirred ball mill or vibrating mill that is used for the size reduction step employs a grinding media comprising zirconia.

42. A method of making a cement paste containing reactive
20 tricalcium phosphate nanoparticles, the method comprising intermixing a lubricating liquid with a cement powder that includes reactive tricalcium phosphate nanoparticles and other ingredients required to form a cementous material.

43. The method according to claim 42, wherein the
25 intermixing is carried out in a time of less than about 4 minutes and at with the ingredients at a temperature of lower than about 10°C.

44. A method of binding articles together comprising:
30 providing a cement paste comprising a lubricating liquid which is intermixed with a cement powder that includes reactive tricalcium phosphate nanoparticles and other ingredients required to form a cementous material;

placing the cement paste at an interface of the articles to be bound together; and

curing the cement paste to form a bond between the articles.

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45. The method according to claim 44, wherein the articles to be bound together comprise the portions of a broken or fractured bone, and where curing the cement paste results in the bonding of the broken or fractured bone.

5 46. The method according to claim 44, wherein the curing step causes a temperature rise in the cement paste which is not harmful to normal living tissues.

47. The method according to claim 44, wherein the temperature rise is lower than about 10°C.

10 48. The method according to claim 47, wherein the curing step is free of the generation of free radicals and wherein curing does not require a toxic or biologically harmful initiator or accelerator.

49. An article that is formed from a biocompatible cured cement comprising the cured form of a cement paste comprising a lubricating liquid which is intermixed with a cement powder that includes reactive tricalcium phosphate nanoparticles and other ingredients required to form a cementous material.

15 50. The article according to claim 49, wherein the article is selected from the group consisting of bolts, nuts, washers, screws, splints, rods, sheets, and cylinders. 112

20 51. A method of storing a calcium-phosphate-type cement paste comprising cooling the cement paste to a temperature that is sufficiently low to preserve the flowability and curing properties of the cement paste so that when the cement paste is reheated to ambient temperature these properties are substantially returned to the state of the paste prior to cooling.

25 52. The method according to claim 51, wherein the cement paste is cooled to a temperature that is below about -20°C for such storage.

30 53. The method according to claim 52, wherein the cement paste is cooled to a temperature of below about -190°C.

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54. The method according to claim 51, wherein the cement paste is cooled to the temperature of liquid nitrogen at ambient pressure.

5 55. Reactive tricalcium phosphate nanoparticles that have been produced by precipitation from a sulfate-containing solution which is free of carbonate and which has a calcium:phosphate ratio of less than about 1.5:1.

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